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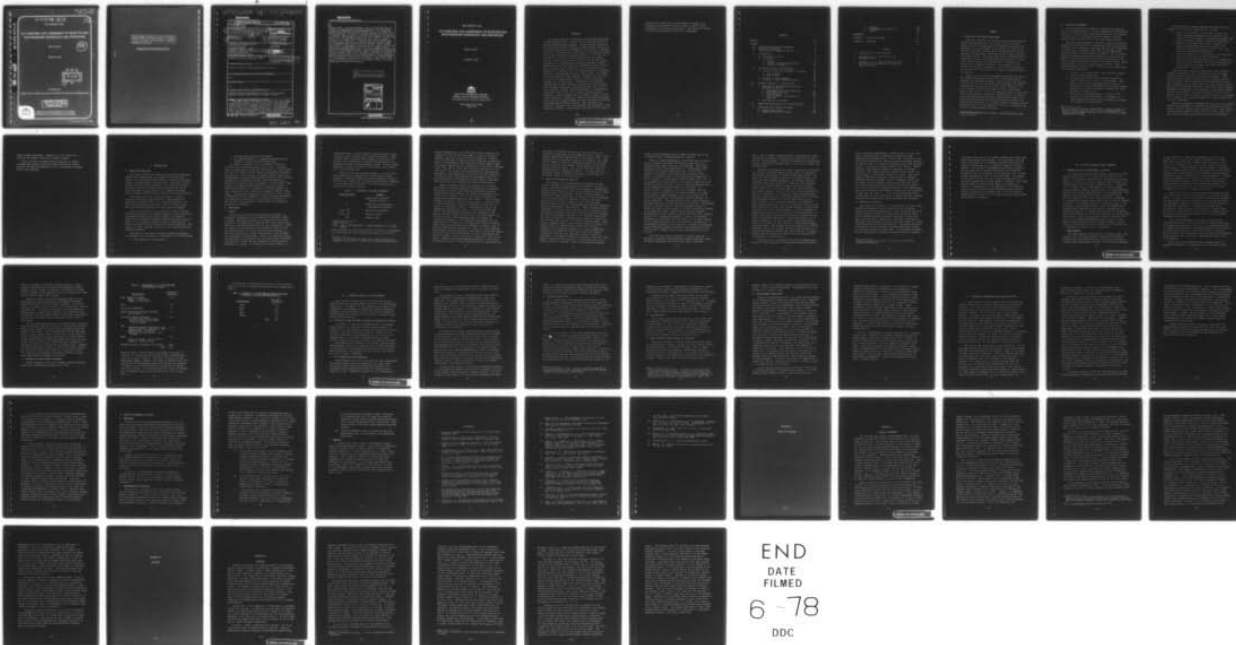
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AN OVERVIEW AND ASSESSMENT OF SELECTED DoD
HIGH-PRESSURE TECHNOLOGY R&D PROGRAMS

John E. Hove

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January 1978



Prepared for

Office of the Under Secretary of Defense for Research & Engineering

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HIGH-PRESSURE TECHNOLOGY R&D PROGRAMS**

John E. Hove

January 1978



INSTITUTE FOR DEFENSE ANALYSES
SCIENCE AND TECHNOLOGY DIVISION
400 Army-Navy Drive, Arlington, Virginia 22202

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ABSTRACT

The Deputy Director for Research and Advanced Technology, ODDR&E, requested IDA to conduct a set of selected studies of the DoD Technology Base Programs in materials and structures. This paper deals with one aspect of these studies, namely the use of high pressures to synthesize or process new or improved materials. The objective of this task is to provide an assessment of the potential application benefits of such R&D and of its chances of success in producing practical and useful results. Over the past decade, the U.S.S.R. has made major investments in high-pressure technology, perhaps an order of magnitude greater than comparable investments made by the U.S. One of the most publicized goals of the Soviet work is the synthesis of a metallic state of hydrogen, which, if feasible, could have very important military implications. The assessment of the present study, however, concludes that this goal is still too scientifically tenuous to justify any major increase in U.S. R&D effort. Nonetheless, the potential national and military benefits are great and a more focused joint research program is recommended between the DoD, NSF, DoE, and NASA. Another closer-term benefit of high-pressure technology could be its use to process and form brittle materials. The techniques used, for example, might be hydrostatic extrusion or explosive. Many brittle materials become quite ductile at high pressures and thus forming at relatively low temperatures becomes possible. This can have very beneficial effects on the microstructure and properties of the resulting component. Since enough basic R&D has been done to

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SUMMARY

A. OBJECTIVES AND GENERAL BACKGROUND

The Deputy Director for Research and Advanced Technology, ODDR&E, has requested that IDA conduct a set of selected studies of the DoD Technology Base Programs in materials and structures. Past IDA papers on the subject have dealt with R&D associated with existing major DoD applications, such as submarine pressure hulls, strategic missile reentry vehicles, and rocket nozzles. This paper deals with a different kind of technology for which proven military applications do not yet exist, namely the use of high pressure* to synthesize or process new or improved materials. The objective of this paper is to provide an assessment of the potential benefits of such R&D and of its chances of success in producing practical results.

Because of its possible long-range potential, the DoD has made modest investments in this area of technology and has achieved some promising advances. However, over about the last 10 years, the U.S.S.R. has made major investments (including a 50,000 metric ton press estimated to have an equivalent U.S. cost of about \$17 million) at least an order of magnitude greater than the U.S. One of the publicized goals of the Soviet work is the synthesis of metallic hydrogen which, if feasible, could have very important military implications. While it is believed that this goal has not been achieved, and while few people would argue that U.S. programs should be driven by Soviet R&D activities, it is reasonable for the U.S. to reevaluate its posture on high-pressure technology.

*For present purposes, this refers to pressures greater than about 30 kbar.

B. TECHNICAL BACKGROUND

From an applications standpoint, high-pressure research has two interesting aspects: (1) the synthesis of new materials which, to be useful, must remain metastable* when the pressure is removed, and (2) the processing and forming of brittle materials which become ductile under high enough pressures.

The best known examples of synthetic metastable materials produced in the laboratory are diamond and cubic boron nitride (Borazon), both of which are very hard and are used extensively for machining. At present, these are also the only useful materials produced by high-pressure synthesis. Of the theoretically postulated new promising materials, certainly the one which has attracted the widest interest and attention is the metallic phase of hydrogen (a lattice of protons bound by quasi-free electrons with no molecular (H_2) preference). With a predicted density close to that of water, the following properties have been speculated:

1. It may be a high-temperature superconductor, perhaps close to room temperature.
2. It should have a high stored energy, estimated as about 30 times that of TNT on a volume basis. This means it may be an outstanding explosive and, if partially or totally controllable, an excellent rocket propellant (a specific impulse is estimated at 1400 seconds) or compact fuel.
3. It will have a hydrogen density of close to 10^{24} particles per cubic centimeter. If useable as a laser fusion fuel particle, it could greatly increase the feasibility of that device.

* For our purposes, the word "metastable" is used to refer to a material crystal structure which is not thermodynamically stable at one atmosphere pressure, but is locked in by a high transformation energy.

Although metallic hydrogen research has great potential benefits, it also has an impressive set of risks:

1. There is no certainty that metallic hydrogen can exist, although something that has a metallic conductivity has been observed for hydrogen between 2 and 6 Mbar by dynamic magnetic compression experiments.
2. There is no certainty that static equipment can reach the required pressures with present anvil materials (although the Soviets claim to have done this in a controversial experiment).
3. It is not known if it can be retained in a metastable state as the pressure is totally released.
4. Even if all the problems cited above are successfully resolved, it is suspected that metallic hydrogen may be very difficult to handle and retain because of rapid surface vaporization.

Aside from pure hydrogen or deuterium, other classes of materials (discussed in the text) have potential for high-pressure synthesis but have not been well analyzed. These form attractive targets of opportunity for research efforts, but will require better experimental data base before intelligent conclusions can be drawn about their chances for success. While most high-pressure-synthesis efforts have involved static experimental techniques, the possibility of explosive synthesis should not be ignored. It is more difficult to control this process (and to keep the sample from being damaged or destroyed) but it promises less costly scaleability to large samples than do static techniques.

From the standpoint of high-pressure processing, successful efforts have been made to form sound fine-textured billets of normally brittle metals, such as tungsten alloys. This type of work has near to mid-term possibilities for new applications and could be especially promising for specialized ceramics

useable in advanced programs (such as development of a ceramic gas turbine). An interesting offshoot of this is the use of transient (e.g. explosive) techniques, still in their infancy, for densifying ceramics. High-pressure forming has sound possibilities for applications with few technological risks.

C. CONCLUSIONS AND SUGGESTED ACTIONS

A summary of the technical conclusions reached in this paper follows.

The probability of obtaining pure metallic hydrogen is still too low to warrant any heavy applied efforts, despite its potential benefits and the spectre of Soviet activities. However, a systematic and steady research program should be maintained (and perhaps strengthened) to resolve the theoretical and experimental barriers to such an achievement.

Greater attention should be given to hydride materials, particularly nonconducting (dielectric) classes of hydrides. There has been educated speculation that "metallic hydrogen" sublattices could be formed at lower pressures (than those required for pure hydrogen) because of dielectric field effects. The author knows of no static experimental high-pressure research that has been performed on dielectric hydrides (e.g., ammonia, ammonium compounds, boron hydrides, etc.) and of very little performed on any hydrides. There has been some shock-wave research on ammonia, however, which showed no surprising results (up to about 300 kbar).

The synthesis of metastable superconducting compounds (other than those containing hydrogen) does not appear particularly attractive. The most promising candidates appear to be Nb_3Si and Nb_3As , since a matrix chart of the critical temperatures of superconducting Nb_3X compounds indicates that these two materials might be higher temperature superconductors than any now known, if only they can be metastably formed in what is

known as the A-15 crystal structure. Attempts to achieve this by high pressure have been made, without confirmed success. There is little reason to believe that such efforts will be successful in the future, although the relatively small efforts underway should certainly be continued. Other techniques (such as sputtering) might be more promising.

High pressure forming and processing techniques for brittle materials, including explosive forming, have good potential for near to mid-term applications and should be accorded a high priority in future R&D planning.

A summary of suggested managerial actions for the DoD is as follows.

A major increase in funding for high-pressure R&D does not now appear to be needed or justifiable. While some areas where small increases and enhanced attention would be useful are pointed out in the text (such as a joint DoD-DoE shock-wave program), the current overall program seems to be approximately the right size, considering the benefits and the risks. By the same token, the potential benefits appear great and care should be taken not to diminish the current level of resources or reduce technological momentum.

Coordination still needs to be improved both within DoD and with other Federal agencies. A permanent coordinating committee, with high visibility, would be desirable.

Since the results of high-pressure research would benefit the nation as a whole, attempts should be made to instigate a reasonably close-knit Federal program. If this is to be done, the DoD probably would have to take the initiative. No other Federal agency has given as much management attention to high-pressure efforts as the OUSDRE. While one possible Federal program is outlined in the text as a strawman, there are many

other possible approaches. However, it is not within the scope of this study to pursue the subject further.

Since the field of high-pressure technology is subject to sudden and perhaps startling changes, the entire subject should be reviewed periodically to see if the present recommendations need changing.

I. INTRODUCTION

A. OBJECTIVES AND SCOPE

The Deputy Director for Research and Advanced Technology, ODDR&E, has requested that IDA conduct a set of selected studies of the Technology Base Program in Materials and Structures of the Department of Defense (DoD). This task is being carried out under DARPA Task Order T-108, which in the past has dealt with R&D of materials and structures for use in major existing DoD applications (i.e., submarine pressure hulls, strategic missile reentry vehicles, and rocket nozzles).

This paper deals with a different kind of on-going materials technology, namely the use of high pressure to synthesize and characterize new or improved materials, for which proven military applications do not yet exist (other than hard synthetic materials for machining and forming).

Thus, the objective of this study is to assess both the potential benefits of the on-going programs and the possibility of producing practical and useful results. An ancillary question to be addressed--assuming high-pressure work is worth doing at all--is how the programs should be organized and split, both within DoD and between DoD and other agencies. The answer, of course, depends critically on the importance of the potential benefits.

The scope of this paper, insofar as program assessment is concerned, will be limited to consideration of the following:

1. The synthesis of new materials

2. The improved processing of materials
3. The characterization of compounds undergoing phase changes or other structural alterations.

In addition, attention will be focused on the use of pressures which are greater than about 30 kbar. The major areas of high-pressure technology omitted by this scope restriction are (1) studies of bond strength and dynamics in crystals and molecules, (2) variations of chemical reaction rates and polymerization kinetics under moderate pressures, and (3) armor penetration or shock-wave mechanics where the material is treated as an elastic-plastic continuum. In these areas, high pressure is simply another laboratory tool used to gain a better understanding of the behavior of matter (however, if phase changes can occur, penetration mechanics remains a grey area). A fourth major area, which is omitted, is that related to geophysics and rock mechanics. While of obvious importance, this area mainly supports the civil engineering efforts of DoD and makes very peripheral contributions to new material synthesis or processing.

B. BACKGROUND

1. General

The practical lure of ultra-high-pressure physics is intimately connected with the phenomena of metastable states of matter. Metastable materials are those that exist under conditions of temperature and pressure which favor some other form (i.e., the equilibrium state) but are, effectively, locked or frozen in. Such materials will eventually revert to the more stable state, but in many cases the time necessary to make the transition (at useful temperatures) can be measured on a geological or cosmic basis. Hence, for human time spans, such materials can be readily used as long as proper conditions are observed. Perhaps the most familiar of such metastable materials are glasses. All glasses will tend to revert to a

crystalline form, a process known as devitrification, which generally tends to destroy their desired properties. High-strength steels and other heat-treatable metal alloys are another class of materials in which vital components (i.e., quenched-in phases) are in metastable states. In such common examples, of course, pressure is not a factor or, at least, not a very important one.

Diamond is far the best-known example of a useful metastable material, the preparation of which requires high pressures. Synthetic diamond was first prepared by General Electric over 15 years ago* at high temperature and a pressure in the 80-kbar range (see Table 1 for unit definition and illustrative pressure ranges).

TABLE 1. ILLUSTRATIVE PRESSURE SPECTRUM*

<u>Pressure (kbar)</u>	<u>Example</u>
1	Deepest part of ocean-- Marianas Trench
10	Mohorovicic discontinuity, crest-mantle interface
1.37×10^3	Mantle-core interface
3.64×10^3	Center of Earth
10^8	Center of Sun

* Taken from Ref. 1.

NOTE: $1 \text{ bar} = 10^6 \text{ dynes/cm}^2 = 0.9869 \text{ atmospheres} = 0.1 \text{ mega pascals}$

After cooling, and when the pressure is reduced to 1 atmosphere, the carbon remains in the diamond structure as long as the

* In fact, the GE patent is about due to expire and this is expected to give rise to a spate of new diamond-making firms.

ambient temperature is less than about 800°C (a diamond ring exposed to a hot fire for any length of time will become a graphite ring, even if protected from oxidation). Shortly after the synthesis of diamond, boron nitride was successfully made in the metastable cubic (diamond-structure) phase, again at elevated temperatures and pressures in the 50-kbar to 100-kbar range. This was the first time any useful material that did not exist in the natural world was man-made by high-pressure processing. Both diamond and cubic boron nitride (marketed by GE under the trade name Borazon) are extremely hard and are used extensively for grinding and cutting wheels, high-speed drill bits, and other machining and forming applications.

These two examples exhaust the present list of *useful* new synthetic materials prepared by high-pressure techniques. There have, of course, been other new metastable materials synthesized at high pressure, but these are considered to be scientific curiosities. Thus, a new cubic yttrium-thorium sesquicarbide superconductor has been formed. A cubic rhenium carbide, not known in nature, has been made. A metallic phase of indium antimonide, normally a semiconductor, has been retained in a metastable state at 1 atmosphere as long as the temperature is below about 200 K. (It should be noted that every III-V semiconductor which has been subjected to high pressure reaches a metallic state, but so far InSb seems to be the only one that stays metastable when the pressure is completely released.) A new metastable cubic phase (not the sought-after A-15 phase) of a niobium-silicon (Nb_3Si) superconductor seems to be obtained after exposure to about 60 kbar at elevated temperatures (see page 19). There are other examples, but the main point that emerges is that these are isolated experiments and a data base broad enough to foster a theoretical predictive capability (for a given class of materials) does not yet exist. Perhaps a systematic Edisonian approach is called for. Furthermore, the use of stabilizing impurities to facilitate the

retention of metastable states can be very important, but theoretical predictions are extremely difficult. Again, a cut-and-try experimental approach may be the most fruitful. Such assembly-line procedures may seem to run counter to what many would interpret as the true scientific method, but at least empirical physical and chemical relationships could be built up which would be useful. This is how the modern state of high-strength-alloy metallurgy grew up. An early, but still pertinent, review of matters relating to the synthesis of metastable states can be found in Ref. 2.

2. Metallic Hydrogen and Hydrides

The possibility of synthesizing a metastable metallic state of hydrogen (with a density of the order of 1 g/cm^3) is perhaps the most intriguing practical problem in high-pressure physics and certainly the one that has attracted the most widespread interest and attention. Since a somewhat detailed discussion of the present state of affairs is given in Appendix A, only a mention will be made here. Briefly, the prime reason for all of this interest is the speculation that metallic hydrogen might be a high-temperature (perhaps approaching room temperature) superconductor. Other potential benefits (although, of course, farther down the scale of interest) are that metallic hydrogen could be an excellent explosive (perhaps 30 times more energetic than TNT on a volume-for-volume basis) and that, in the form of deuterium and tritium, it could be a very efficient fuel pellet for the laser fusion process. Thus, metallic hydrogen seems to offer great potential benefits. Of course, there are a few problems, which are discussed in Appendix A and summarized in Section IV. Even assuming that metastability is possible, there will still be problems of containment, handling, and reasonably economic production techniques. For example, pressures of between 1 Mbar and 5 Mbar might be required, and the anvils of the pressure cell would probably have to be diamond. Since carbon-hydrogen reaction

rates at these pressures are not known, this may prove to be an expensive way of making methane or acetylene.

From all outward appearances, the Soviets take the possibility of metallic hydrogen very seriously and seem to be applying rather heavy resources to the problem. There were statements by the late academician L. F. Vereshchagin (then Director of the High Pressure Institute of the U.S.S.R. Academy of Sciences) to the effect that the famous 50,000 metric ton research press at the Institute was designed and built primarily to investigate metallic hydrogen (Ref. 20). It is estimated that this huge piece of equipment would have cost about \$17 million if built in the U.S. (and considerably more if all auxiliary facilities were to be included). As a matter of fact, it appears to most U.S. observers that the press is much too large for only research purposes (a larger press produces larger specimens, but if all one wants to do is measure properties, a large sample, though convenient, is hardly essential). One speculation is that a major purpose of the press might be for large hydrostatic extrusions. Vereshchagin has publicly stated that the metallic hydrogen transition (where, in effect, solid H_2 goes to a solid $2H$) has been observed in an experiment using a smaller press, although complete metastability was not claimed as the pressure was fully released. As more fully discussed in Appendix A, there is controversy regarding this experiment and the matter is by no means settled. It is interesting to note that very impressive obituaries to Vereshchagin appeared in both Izvestia and Pravda; one mentioned metallic hydrogen synthesis among his accomplishments and the other did not. Perhaps there is also controversy within the U.S.S.R.

Since the most intense interest in metallic hydrogen involves its possible high-temperature superconductivity, there has been considerable speculation that similar desirable

effects may be found in hydrides without encountering as great difficulties in making the materials as would seem to be the case for solid hydrogen. Appendix B discusses the possibilities involving hydrides in moderate detail; thus, only a summary will be given here.

Compounds of hydrogen with metals, particularly the transition metals, have been studied for many years in connection with nuclear technology and energy storage applications. The reason for this interest is that many of these materials can have quite high hydrogen densities. For example, titanium dihydride (TiH_2) has nearly 10^{23} H atoms per cm^3 , reasonably close to the predicted density range of metallic hydrogen itself (about $4-8 \times 10^{23}$ H atoms per cm^3), and much greater than liquid hydrogen. Thus, in the late 1960s [influenced by Ashcroft's speculation on the possible high superconducting critical temperature, T_C , of metallic hydrogen (Ref. 3)] there were widespread attempts to look for superconductivity in metal hydrides at one atmosphere pressure. No spectacular results were obtained and, in fact, no positive results at all were obtained until 1970, when a higher hydride of thorium was found (Ref. 4) to be a superconductor. In 1972, hydrides of palladium and its alloys were found to be superconductors. It appears that these are the only two hydride systems presently known to show superconductivity. While their behavior is of extreme interest to the basic theory of superconductivity, there is no evidence of the formation of a metallic-hydrogen-like sublattice. Both systems have been subjected to moderate pressures (20 kbar to 30 kbar) but, until very recently, no serious high-pressure research has been conducted. It should be mentioned that these also appear to be the *only* hydrides investigated at high pressures.

Dielectric (i.e., nonconducting) hydride compounds have had very little unclassified high-pressure research attention

(mainly shock-wave experiments on ammonia, Ref. 5), yet could form a promising group of materials for potential high-temperature superconductivity. Gilman (Ref. 6) points out that the pressures required for forming a metallic-hydrogen lattice may well be lower in a dielectric hydride than in pure hydrogen, because of the lattice internal dipole field effects. Gilman analyzes a hypothetical compound (a dihydride of lithium fluoride). His numerical results appear to be in error*, but the principle of his argument seems to be sound. There are a number of dielectric materials which could be of interest, including ammonium compounds (as well as ammonia itself) and the series of boron hydrides, starting with diborane (B_2H_6). The latter system of hydrides could be of special interest, since recent (and still tentative) results on the high-pressure behavior of elemental boron appear to show a metallic transition at about 450 kbar (Ref. 7). It is only educated speculation at this time, but the possibility of forming dielectric hydride superconductors seems great enough to warrant R&D attention.

3. Materials Processing

Aside from the synthesis of new materials, the other high-pressure technological area of interest is in processing brittle and hard-to-work materials. The only process which has received much DoD attention is hydrostatic extrusion, where typical maximum extrusion pressures have been 15 kbar and 20 kbar. Even at modest temperatures, difficult-to-manufacture materials, such as tungsten alloys, have been formed into sound, fine-textured billets by this technique. Reasonable ductility is observed at these pressures, and undesirable grain growth and chemical reactions are minimized. An interesting extension would be hydrostatic extrusion of ceramic materials, although

* Private communication from C. F. Cline of the Lawrence Livermore Laboratory.

nothing has been done so far (largely because much higher pressures would probably be required). The Department of Energy (DoE), particularly at its Lawrence Livermore Laboratory, is looking at shock-wave (i.e., explosive) forming of ceramic powders. This has been investigated sporadically during the last 30 years, but no serious applications have resulted. Presumably, part of the reason is the high piece-cost of such forming compared with that of other techniques. For example, in the case of metals, the only commercial applications of explosive forming have been the making or welding of very large complex shapes, for which other types of processing are difficult. Nonetheless, if the properties of the resulting ceramic body can be sufficiently improved by high-pressure forming, there may be an economic case to be made for such newer structural ceramic uses as high-performance seeker domes or gas-turbine components.

II. EXISTING TECHNOLOGY BASE PROGRAMS

A. PROGRAMS WITHIN THE DEPARTMENT OF DEFENSE

As indicated in the resource summary in Section C of this Chapter, the total FY 1977 estimate of DoD funding for all types of high-pressure technology R&D (excluding that for geophysics) is about \$3.4 million. However, this overview is not concerned with research using pressure merely as a laboratory tool to further a basic understanding of crystal bonding, lattice dynamics, chemical reaction rates, or other fundamental physical and chemical characteristics of known materials. Such work can only be judged on the basis of the goals of the projects themselves; the use of high pressure is incidental. As a knowledgeable reader might expect, most of the \$3.4 million is spent on such research, which is outside the scope of this discussion. The estimated portion of the DoD high-pressure technology R&D resources devoted either to seeking out new high-pressure phases of elements and compounds or to investigating new high-pressure processing techniques is actually about \$1.3 million. Most of this is being spent by the Army, with little or no current expenditures by the Air Force or the Defense Advanced Research Projects Agency (DARPA). In the following discussion, only the synthesis and processing types of high-pressure projects will be referred to.

1. Army Programs

The high-pressure technology R&D in the Army tends to be concentrated in the Benet Weapons Laboratory at Watervliet Arsenal, which the Army describes as "the largest and most broadly based high-pressure research and technology laboratory

in the free world." While this statement may be true, the organization is still fairly modest, consisting of a little more than 15 professionals, somewhat fewer technicians, about 20,000 ft² of physical plant, and an annual budget of around \$800 thousand. It does, however, have an impressive and modern array of pressure generation and containment research facilities, together with a good experience in calibration and measurement techniques, both at cryogenic and at high temperatures. Included among the equipments are a 20 kbar to 40 kbar system, used to study hydrostatic forming, and two relatively large-volume presses dedicated solely to ultra-high-pressure research (one system is now routinely used close to 500 kbar and another, designed for 1000 kbar, is under construction).

Until very recently, the Army high-pressure programs have had a low profile within the DoD and almost no profile outside, except, of course, for some individual scientists and engineers. The work started (logically enough for the Army and especially for Watervliet Arsenal) as a study of autofrettage techniques for large-bore gun tubes. Autofrettage pressures are not particularly large, perhaps in the 10-kbar to 20-kbar range. In about 1972, the work of building up the ultra-high-pressure facility at Watervliet began and by about 1975, the 500-kbar system was in operation.

A few recent highlights of the Benet program are the confirmed discovery of very high electrical conductivities (in the temperature range of 30 K to 50 K) in a high-pressure phase of bismuth which may imply a new high-temperature superconductor; the apparent discovery of a new metallic phase of boron at about 450 kbar; and a beginning of an investigation of palladium-alloy hydrides, the first serious high-pressure study of any of the hydrides.

There seems little question that the Benet activity is vigorous and likely to be productive from a scientific basis.

It is probably true that, at this stage, more money would not help the Laboratory achieve its goals. It does appear, however, that it could use stronger management encouragement if it is decided that such work should be done in DoD at all.

The Army Research Office is also sponsoring inorganic synthesis projects at Rice University. This work was funded at about \$200 thousand annually.

2. Navy Program

The Navy has a small group at the Naval Research Laboratory (NRL) doing high-pressure research, up to about 60 kbar at temperatures of less than 1 K. Using about three or four professionals, this effort is part of a larger cryogenic program, and concentrates on superconducting compounds. Among other activities, efforts have been made to synthesize a metastable form of Nb_3Si (i.e., the A-15 structure) which has been speculated to have high-temperature superconducting characteristics. Such efforts have not been successful, but the problem is difficult and the issue not yet clear. An unidentified metastable cubic phase of Nb_3Si has apparently been obtained after exposure to about 60 kbar and 1400°C . However, this had no interesting properties. A combination of the Office of Naval Research (ONR) and DARPA has been sponsoring an effort at UCLA to synthesize stronger polycrystalline forms of diamond, one form of which is sometimes called carbonado. The results of this work could have applications, among other things, to better high-pressure anvils, an area in which the Soviets are thought to excel over the U.S.

These efforts have a total annual funding of, perhaps, \$350 thousand.

B. PROGRAMS OF OTHER AGENCIES

The resource summary in Section C of this Chapter indicates a total FY 1977 high-pressure expenditure of about \$9.9 million for all government agencies other than DoD.

By far the bulk of this, \$8.7 million, is the funding ascribed to DoE at Sandia Laboratory, Los Alamos Scientific Laboratory (LASL) and the Lawrence Livermore Laboratory (LLL). The writer has not made a detailed study of these projects and thus finds it difficult to assess just what fraction of this funding is currently applicable to new-material synthesis and processing.

In the past, the weapons laboratories have made significant contributions to synthesis. About 8 years ago, the Los Alamos Group (Ref. 8) did some very interesting work on synthesizing new, metastable thorium-yttrium-carbon superconductors. This work no longer appears to be going on. In the period ending about 2 years ago, LLL was still working on static high-pressure experiments involving lithium hydride and ammonia. About 2 years ago, Hawke and colleagues (cited in Ref. 9) of LLL did some elegant magnetic field compression experiments on hydrogen and observed a metallic-like electrical conductivity at a pressure estimated between 1.5 and 6.0 Mbar. Unfortunately, these results could not distinguish between a true phase change and other possible competing mechanisms (a general difficulty of many dynamic experimental techniques). These LLL projects apparently are no longer being actively pursued, perhaps due to a general reappraisal by DoE of its R&D priorities. A perusal of some LLL publications over the last 3 years, pertaining to high-pressure research shows that the overwhelming bulk (30 papers out of about 40) deal with geology and rock mechanics, which are subjects outside the scope of this study. The R&D capability in the DoE national laboratories for advanced high-pressure synthesis and forming is very large. It is generally not being used at present. The only on-going work at the laboratories which the writer could identify as applicable to this study is a small effort (perhaps \$200 thousand annually) to explosively form materials, especially amorphous metals. Also, a new program is being initiated at Los Alamos to grow single crystals of certain plutonium phases

under high pressure (about \$80 thousand annually). Since probably something less than half of the Materials Sciences Program contract support is pertinent to synthesis, the best current estimate of DoE expenditures which lie within the scope of this study is about \$500 thousand.

NASA has a small in-house high-pressure effort at the Lewis Research Center (focussing on the metallic hydrogen problem) and two or three university contracts. One of the latter, at Cornell, is for a study of the transition(s) in boron phosphide (BP). As with all the other III-V semiconductors investigated, a high-pressure transition to a metallic state is expected. The total NASA effort is estimated at about \$500 thousand and is probably mostly applicable to the scope of this report.

The work being sponsored by the National Science Foundation (NSF)--about \$500 thousand, exclusive of geophysical studies--does not seem relevant to any of the technological goals discussed in this paper. The writer believes that the NSF ought to play a more vigorous role, a point that will be touched on later. Similarly, the present high-pressure research effort at the National Bureau of Standards (NBS) (which has been very active in the past) is small, excluding their standards and calibration function, and will not be discussed here. However, the writer would like to mention a small NBS program studying the theoretical statistical mechanics of metastable states. This could be very promising, since metastability is really what high-pressure synthesis is all about.

C. ESTIMATE OF TOTAL PRESENT RESOURCES

Table 2 summarizes the *stated* funding estimates from all sources for high-pressure research in FY 1977.

TABLE 2. APPROXIMATE FY 77 HIGH-PRESSURE
R&D RESOURCES (TOTAL)

<u>Organization</u>	<u>Millions of Dollars</u>
Army (mostly in-house) Benet - 0.8 million Others - 0.6 million	1.4
Navy	2.0
Air Force (presently)	0
DARPA (excluding programs completed during year)	0
National Science Foundation (an additional Earth Sciences effort of about 0.8 million is not included)	0.5
DoE Lawrence Livermore Laboratory, Los Alamos Scientific Laboratory, Sandia Laboratories - \$8 million Materials Science Program - \$0.7 million	8.7
NASA Lewis (in-house) - \$0.24 million Contract - \$0.26 million	0.5
National Bureau of Standards (currently)	<u>0.2</u>
TOTAL	13.3

Note that Table 2 was obtained by requesting the sources to estimate all contractual and in-house efforts involving pressures of at least a kilobar. The total, as seen, is a very respectable figure. However, this study is concerned only with work which has technological bearing on new material synthesis or high-pressure processing where the pressures are greater than about 30 kbar. All additional work has other (and presumably legitimate) objectives and, therefore, is not an issue here.

As discussed in the previous two parts of this Section, funding estimates of such applicable efforts are summarized in Table 3.

TABLE 3. ESTIMATE OF FY 77 HIGH-PRESSURE RESOURCES APPLICABLE TO NEW-MATERIAL SYNTHESIS AND PROCESSING ONLY

<u>Organization</u>	<u>Millions of Dollars</u>
Army	1.0
Navy	0.4
DoE	0.5
NASA	0.5
Others	0
TOTAL	<u>2.4</u>

III. POTENTIAL BENEFITS OF APPLICATIONS

Here, we shall discuss some of the potential practical benefits that can be speculatively foreseen from high-pressure R&D results. Although of obvious importance, increases in our fundamental understanding of solid-state physics, chemistry, geophysics or astrophysics, as such, will not be considered. The discussion will be split into two parts, synthesis of new material and processing.

A. SYNTHESIS OF NEW MATERIALS (METALLIC HYDROGEN AND OTHERS)

This refers to new crystallographic phases of elements, known compounds, or presently unknown compounds which are stable only at high pressures such as the hypothetical metallic hydrogen. Such materials would normally be useful only if they were metastable at one atmosphere, or, at least, a low enough pressure to constantly maintain during use (which could be several kilobars by utilizing an ice-bomb technique).

Such new-material synthesis would probably require ultra-high-pressures, since it is probable that if useful materials could be formed at moderate pressures they would already have been discovered. The possible inherent error in this statement is, of course, recognized.

1. High-Temperature Superconductors

"High-temperature" in this case refers to any superconducting material with a critical temperature, T_C , above about 30 K, where liquid hydrogen cooling can be utilized and a reasonable current density maintained (the highest T_C now known is 23.2 K). Assuming it exists and can be maintained,

speculations on the T_C of metallic hydrogen range as high as 240 K, or nearly room temperature (and, to be fair, as low as 0 K).

The synthesis of such a high-temperature superconductor would represent a technological breakthrough of the first magnitude. The biggest impact would be in avoiding joule heating (I^2R) losses in domestic electric power transmission and distribution lines. The theoretical energy (and hence cost) savings here can be enormous. It is possible to come up with estimates of almost \$20 billion per year wasted due to line losses alone. Net savings, by using superconductors, are another matter, since they depend on material and installation costs, but it is clear that the economic incentive could be large. An added bonus would be the increased flexibility in choosing electric power generation sites *vis-a-vis* the locations of the consumers.

In large-scale electrical power generation, applications to magneto-hydrodynamic (MHD) machines are obviously important in the near term. In the longer term, some types of nuclear fusion machines require high magnetic fields. Less obvious, but of great significance to the DoD, are the applications for high-energy-density primary and auxiliary power units of ships and aircraft (Ref. 10). For example, it has been estimated that the use of a superconducting electric drive can decrease the fuel consumption of destroyer-size ships by up to 25 percent. MHD auxiliary power generators (as well as superconductive rotating machinery) for aircraft use have been intensively studied; clearly, a major feasibility problem is the weight (and volume) of the cryogenic system.

Non-power DoD applications include electromagnetic weapons and super-directed antennas (which are not considered practical at the moment, partly because of conductor losses). The list could go on, but there is little point in belaboring the issue.

There is no doubt that a practicable high-temperature superconductor would have tremendous impact; the bulk of the applications, of course, would reflect National and DoE goals, but these for the DoD alone are still of great importance.

2. Explosives and Fuels

On a volume basis, the predicted stored energy of metastable hydrogen is estimated to be about 25 to 30 times that of TNT. If this can all be recovered by some means of deliberate activation, the material could be an outstanding explosive, a fact which has not escaped the attention of the Soviet researchers. If the reaction can be even partially controlled (say, by finely dividing the material), then applications could include rocket motors. In an optimistic mode, one can envision performance equal to or better than the Nerva rocket concept* without all the problems of nuclear hazards. Similarly, potential applications to long-range ballistic missiles are obvious.

To a lesser extent, all the above applications could be benefited by a metallic-hydrogen-like hydride material. This may actually be a more interesting possibility, since the chances of actually being able to control the reaction should be greater. If the reaction could be totally controllable, a new and very large realm of applications would open up involving heat sources for compact power supplies. A variation of this, the use of hydrogen fuel for ground vehicle engines, has been under study for many years and was one of the reasons behind past hydride R&D. The practical hazards of high pressure and temperature have pretty well prevented any serious use of

* As a matter of fact, Ref. 11 quotes a specific impulse for metallic hydrogen of 1400 seconds, which is some 60 percent better than the nuclear rocket engine.

hydrogen in this manner. Conceptually, the existence of metastable hydrides, with very high hydrogen densities, could introduce new avenues of approach which may avoid these problems.

Another type of "fuel" application exists in the laser fusion program of DoE. Here the imploded hydrogen-isotope density must be of the order of 10^{26} particles per cm^3 . Assuming that the densities are about the same as for hydrogen, metallic phases of deuterium and tritium would have particle densities only about a factor of 100 to 300 less than this. This could have a major influence on the feasibility of laser fusion.

3. Hard Materials

Even though a great deal has been done in this area, only two materials (carbon and boron nitride) have been examined at high pressure.* None of the other compounds, normally considered hard materials, has been deliberately exposed to pressure experiments (except perhaps for some Soviet work on aluminum nitride). This should not be ignored, although the writer cannot suggest a directed course of action.

4. Other Potential Applications of Synthesis

There are a number of possible applications which cannot be made definite at present, because they have not been investigated sufficiently. Reference 2 discusses a few of these, including new catalytic, magnetic, luminescent, and ferroelectric materials. Unfortunately, no one seems to have any specific ideas, so such applications must fall in the "blue-sky" category. However, at least one reason why there are no

* These systems can be complex. For example, aside from the known crystallographic phases of carbon, there appear to be a number of so-called transient metastable states which may play a part in attempts to sinter polycrystalline diamond. A recent pertinent reference is Derjaguin et al., (Ref. 12).

specific ideas is that applied research in high-pressure technology is still not very widespread. Serendipity has not yet had much of a chance to work.

B. HIGH-PRESSURE PROCESSING

Using ultra-high-pressure as a tool, many brittle materials can be densified and reshaped with remarkable ease. High-alloy steels, tungsten alloys, and uranium alloys have been hydrostatically extruded at low temperatures (even room temperature) into dense, fine-textured billets with a highly uniform property distribution. Pressures involved were of the order of 15 to 20 kbar. At these pressures, the materials tend to flow ductily, but with little or no grain growth or impurity/phase agglomeration. Of rather obvious potential importance would be a similar ability for ceramic materials, but such R&D does not seem to have been seriously conducted. The pressures would have to be higher, of course, since even the most "ductile" structural ceramic still has less ductility than what are normally called brittle metals. At least one reason for the past low interest in high-pressure processing of structural ceramics has been the low usage of such materials. In almost all past structural applications (concrete, to use a down-to-earth example), the material has either been prestressed or used in such a fashion that the formation of cracks was not harmful. This situation is now in a state of rapid flux. For example, both DoD and DoE have projects on ceramic use in engines, such as gas turbines, where the material cannot be prestressed and cracks cannot be allowed to form and spread. In view of such changes in application viewpoints, R&D into high-pressure forming of ceramics should have a high priority in the future.

Optical windows for such uses as high-power lasers form a potential application of high-pressure forming. To resist thermal stress effects (which, in some cases, may be a

power-limiting factor), a polycrystal (as opposed to a single crystal) window would be preferable in such materials as magnesium fluoride, but, of course, the transmissivity would then not be high enough. It is conceptually possible to make polycrystalline bodies by ultra-high-pressure forming, which should be as transparent to optical, IR, or RF frequencies as a single crystal. Note that this is not necessarily limited to enhancing the strength over a single crystal. Other properties, such as thermal conductivity, may be preferred in a given material, but large single crystals of that material cannot be grown, so another material (with less desirable properties) must be used. For example, beryllium oxide would be a much more reliable high-power klystron window, but sapphire must be used, since single crystals of sufficient size are available. It appears that there are a number of specialized window applications where high-pressure forming could have strong benefits.

The use of high-pressure, high-strain-rate (i.e., explosive or shock wave) forming is a well-known commercial process for making large, complex metal shapes out of sheet or plate. On the other hand, there has been little exploratory work on the use of such techniques for forming powders to near-net final shape. Some work is underway (at Lawrence Livermore Laboratory) to make monolithic or laminated pieces of amorphous metals where the temperature must be kept low to preserve their metastable state. For the same reasons mentioned previously, it would appear advantageous to explore this technique with respect to ceramic powders.

IV. POTENTIAL TECHNOLOGICAL AND PRACTICAL RISKS

For applications involving high-pressure processing and forming, there are few technical risks in the usual sense of the word. It is well known that such techniques will work (although there may be some problems such as subsequent residual stresses). The real risks are practical and/or economic. Equipment costs will be high and thus applications must exist for which the enhanced performance of the material is worth the cost. Furthermore, one must be concerned with the shape being formed, especially for ceramic materials. If near-net shapes are not obtained, extensive machining will be necessary which will further drive up the cost. Close collaboration with the system or component designer is essential, since joints and fasteners are always a serious problem with brittle materials. While they must be seriously considered from the outset, these are all superable problems which are not real obstacles to the performance of exploratory work.

The synthesis of new materials is another matter. It is not known whether any useful new materials (other than diamond and cubic boron nitride) can be man-made. There are not even any good theoretical techniques, other than educated intuition, for predicting where and how to look for such materials. It should be recalled that for a new phase of an element or compound to be useful, not only must properties show some benefit, but the material must be metastable at very low pressures in a practicable temperature range. Much data is available indicating interesting phase changes at high pressure in a wide range of materials, but, to date, only about a half-dozen of these phase changes have been retained when the

pressure is released. If this is not accomplished, high-pressure research is useful for increasing basic knowledge of physics and chemistry, but little else.

An example of this uncertainty can be given for metallic hydrogen, which has had more attention than most potential new materials, partly because of its seemingly simple structure and partly because of its possible (and high) applications value. Free energy predictions of the pressure at which the assumed metallic state becomes stable have varied from a little less than 1 Mbar to almost 20 Mbar, although many people believe this should be narrowed to about 2 to 4 Mbar. However, this prediction assumes a normal metallic structure. Concerns have been expressed that some form of quantum material might result, in which case "metallic hydrogen" (in the normal sense) might not exist. There have been both dynamic and static experimental reports that some type of metallic-appearing material has been observed at pressures thought to be in the above range, but it has never been clear just what has been observed. If the assumed metallic state exists, it may or may not be metastable at one atmosphere (cohesive energy calculations indicate it could be). One prediction (Ref. 15) suggests that even if metallic hydrogen is metastable, a sort of runaway surface vaporization might take place in a relatively short time, partially due to light nuclei tunnelling effects. Thus, the situation exists in which it is not clear whether the phase exists, whether it is metastable, or whether it can be handled or used if it is. Clearly, the technological risk is high. In the author's judgment, based on the critique in Appendix A, our scientific understanding of metallic hydrogen is still too poor to justify any major increase in resources devoted to its synthesis.

In addition, there is a practical manufacturing risk associated with metallic hydrogen or any other metastable material

synthesized at ultra-high pressures. To be economically useful, the material must be producible in quantity. To use high-temperature superconductors as an example, the conceivable applications would require many tens of kilograms per year for very specialized use, ranging to many tens of tons per year for transmission line use. A typical multi-million dollar press could produce, at most, a kilogram or so per year under good conditions. Thus, such a press, while useful for research, is not likely to be used as a production tool. One must go to some other technique, such as crystal growth from seed crystals produced under ultra-high pressure. However, the development of such techniques would require further research programs which cannot even be formulated until the success of primary research yields the required metastable material.

Clearly, the R&D programs discussed in this paper (for high-pressure synthesis) are only the first step; the second step, to develop practical production techniques, may prove to be as difficult and risky as the first step, although the problem will be better defined.

V. CONCLUSIONS AND SUGGESTED ACTIONS

A. GENERAL CONCLUSIONS

The following set of conclusions appears to be justified by the previous discussions.

1. *For the pure metallic hydrogen problem, a moderately paced systematic and balanced basic research program, using both static and dynamic techniques, appears to be the best approach.* In particular, the pressure-volume-temperature behavior of solid molecular hydrogen should be mapped over a wide range of the variables, with pressure extending to the order of hundreds of kilobars. Despite the apparent high potential benefits and the apparent spectre of Soviet activity, it is not yet time for an expensive, focused crash effort. The probability of obtaining a useable metastable metal is too low to warrant a heavy applied concentration. The Army Benet Weapons Laboratory work on argon is a possible precursor to later hydrogen work, even though argon is much less compressible than hydrogen. This effort should continue at a steady pace using the present equipment capability up to about 500 kbar. The experimental work at Lawrence Livermore Laboratory on magnetic compression, which attempted to observe the hydrogen metallic transition (and which had a qualified success about 2 years ago), is not being continued. Possibly, this action is technically justified in that little more can be learned definitively from such experiments, but this is not clear and a further DoD-DoE consensus should be sought. Along with experimental studies of the molecular hydrogen equation-of-state, additional theoretical computations seem essential.

A crucial point is that, even if all the metallic hydrogen research results were positive, producing the metal in useful quantities represents a difficult (perhaps impossible) research effort requiring innovative ideas more than dollars. To speculate more on this problem before knowing whether the metastable metal exists would, of course, be premature. However, one conclusion can be drawn from the inference that static ultra-high-pressure equipment is not adaptable to economic production techniques; a very large press (akin to the Soviet 50,000 metric ton press) is an expensive and unnecessary luxury for synthesis research at ultra-high pressures. Property measurements can be made on a cubic-millimeter sample.

2. *High-pressure work on hydrides presents a seemingly attractive target-of-opportunity for the possible development of high-temperature superconductors, even though the work cannot presently be focused very definitely.* Research on dielectric (i.e., nonconducting) hydrides appears to be virgin territory, since all high-pressure work to date (known to the writer) has been on the hydrides of thorium and palladium alloys. Reference is made to the prediction that a hypothetical dihydride of lithium fluoride should exist where a metallic hydrogen sublattice might be formed at comparatively low pressures (Ref. 6). This idea postulates a strong internal dipole field effect and, in principle, can be extended to any dielectric hydride. Additional examples which seem to have potential interest are given in Appendix B. If such hydrides could be formed at lower pressures and show a high superconductivity critical temperature and a high stored energy, they have the overwhelming potential advantage of being economically producible (as a rough rule-of-thumb, pressures of the order of 100 kbar to 200 kbar or less are amenable to more or less practical production methods).

3. *The attempt to synthesize metastable superconducting compounds (other than those containing hydrogen) does not seem to be particularly attractive.* The Naval Research Laboratory has investigated one potentially promising lead, that of transforming Nb_3Si into the β -tungsten (A-15) crystal structure which was speculated to have a critical temperature of 30 K or greater. However, the results were negative. At this time, there appear to be no guidelines for proceeding with the search for new high-temperature superconductors through the use of high pressures. Obviously, an open mind should be kept for future discoveries.

4. *High-pressure forming and processing techniques, especially for brittle materials, have potential for near- to mid-term applications and should be given a high priority in DoD R&D program planning.* Good work has already been done on processing high-strength steels, tungsten alloys, and uranium alloys by hydrostatic extrusion in the 15-kbar to 25-kbar range. It is interesting to contemplate similar processing methods (albeit at higher pressures) for refractory ceramic materials. This will probably result in high costs per piece, by ordinary ceramic standards, but for some potential applications (such as the ceramic gas turbine) projected competitive costs may be even higher. The DoE has a fledgling expertise in explosive forming of ceramics and this should be nurtured in some cooperative way between DoD and DoE. A general economic problem in making high-performance ceramic bodies is machining. It is thus important, after the basic feasibility of plastic deformation processing has been shown, that such techniques be engineered to produce pieces of near-net shape. Other problems, such as joining, will arise. However, if high-pressure processing cannot produce ceramic bodies with truly enhanced properties (especially from a fracture mechanics point of view), the other problems will be of no concern.

B. SUGGESTED MANAGERIAL ACTIONS

1. Resources

In the area of ultra-high-pressure synthesis, it is not clear that any major increased DoD funding would be useful in the near future. With some exceptions, the on-going programs are opportunistic, and this is as it should be for the moment. Some additional research effort should be planned for investigating dielectric hydrides (including ammonia and its compounds) which show promise. However, before any major additional resources can be intelligently justified, the experimental data base and theoretical understanding surrounding metastable compounds must be expanded. Major in-house equipment seems adequate and progress is still largely limited by ideas and good fortune.

However, the potential benefits of such research to the DoD, although difficult to quantify now, appear great, and care must be taken not to decimate the present resources or reduce the present technological momentum, at least until the program has matured sufficiently to allow a more rigorous assessment.

In the area of high-pressure processing, additional program planning should be made to consider the forming of ceramic bodies. As part of this planning, a joint program between DoD and DoE on explosive forming should be seriously contemplated.

2. Organizational Interaction

Until recently, coordination of high-pressure efforts within DoD was weak and between DoD and other Federal agencies almost nonexistent. In fact, it was only about a year ago that DoE shock-wave experts and the DoD and NASA static pressure experts began to talk to each other, although, of course, there were individual exceptions. There have been enough instances

in which one service was not aware of high-pressure work in another that a permanent coordinating committee for the DoD seems highly desirable. This would also provide a focal point for interaction with other governmental agencies both in coordinating and formulating joint programs. This latter point is important, since much of the potential value cited for high-pressure research is of benefit to all Federal technical agencies. In fact, attempts should be made to organize a national program, both because resources would be better utilized and because some portions fall more naturally within the purview of one agency or another, either because of charters or existing facilities. One possible option for such a program, without regard to any competing interests which may exist, could be as follows:

- (a) As the major grant agency for basic research, the National Science Foundation would focus on large-machine computational methods to improve the theory of insulator-metal transitions as a function of pressure and temperature. While this is a general problem in mathematical physics, hydrogen should be the first material to concentrate on, both because it is one of the simplest and because of its potential national importance.
- (b) In coordination with the NSF program, DoD, DoE, and NASA would plan a systematic experimental program on the equation of state of molecular hydrogen over as wide a range of pressures and temperatures as possible.
- (c) A "pot-boiler" type of experimental program, covering a range of materials, would be planned to provide a better general data base for high-pressure synthesis. The lack of such an extensive data base is one of the obstacles to formulating

a better predictive theoretical model. Materials to be tested would not, of course, be picked at random but should follow "educated guess" guidelines, such as those presented earlier in this paper. This could be part of the Army's Benet Weapons Laboratory program.

- (d) The DOE shock-wave facilities would provide such measurement input to the program as are needed and agreed upon.

3. General

The writer would like to make a brief general comment about ultra-high-pressure research. Aside from the foreseeable practical aspects, there are great benefits in having the research capability to achieve pressures up to 1 Mbar or more. This is a valuable tool in understanding the basic physics of materials. Such capability exists, or shortly will exist, together with assembled scientific teams to perform and interpret the experiments. It is strongly recommended that, by whatever means, this capability be maintained. To allow it to disintegrate would create a major gap in the national materials physics research capabilities which would be difficult to fill.

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APPENDIX A

METALLIC HYDROGEN

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Over 40 years ago, Wigner and Huntington (Ref. 13) first predicted the possible existence and properties of a metallic phase of hydrogen. Such a phase would only be stable relative to molecular H_2 at very high pressures (of the order of a Mbar), but if its binding energy were high enough at constant volume, the hope was that it would remain metastable as the pressure was lowered to one atmosphere, much as diamond is metastable under room conditions. Regarded largely as a theoretical curiosity which was mostly useful to astrophysicists, metallic hydrogen was investigated at a slow pace until the 1960s. Then, in 1968, Ashcroft (Ref. 3) presented some calculations of the critical temperature (T_C) for superconductivity in the hypothetical metallic phase. Although Ashcroft was suitably cautious, it is possible to deduce a T_C of over 200 K from his results. Thus, if the metallic phase were indeed metastable at room temperature and pressure, the possibility existed that it might be a superconductor at close to room temperature.

Since a usable room temperature (or even greater than 30-K to 40-K) superconductor would have revolutionary practical implications, interest in metallic hydrogen escalated. Clearly, a key requirement is that the metal phase be metastable at one atmosphere (or at least nearly one atmosphere). Calculations of the equation of state (Ref. 14) at zero temperature indicated a positive binding energy, for the metal phase, of about 0.8 eV/atom relative to H atoms. Reference 14 also predicts the zero-pressure density as 0.57 g/cm^3 . Since 0.8 eV/atom is a high

cohesive energy for the metastable state, this would appear to suggest that the metal phase might exist at room pressure and temperature. Unfortunately, this conclusion may not be correct. Salpeter (Ref. 15) calculated the order of magnitude of the "evaporation" of surface atoms (to form H_2 molecules) by both quantum mechanical tunnelling and thermal effects. Because of the low mass of the hydrogen, quantum barrier penetration effects are important. Salpeter concludes that "evaporation" could proceed in a sort of autocatalytic reaction which will eventually result in a "thermal runaway", destroying the metal crystal. He actually calculates a lifetime of ~ 100 seconds for a macroscopic crystal in a vacuum, but points out that this might easily be ~ 1 msec. The isotope effect of replacing H by D is, of course, enormous, and solid deuterium should be much more stable. Furthermore, pressure effects should also inhibit this reaction.

Over the last 5 years there has been an enormous effort in ultra-high-pressure research by the Soviet Union (Refs. 16, 17, 18). A good bibliography of Soviet papers related directly to metallic hydrogen is given in the recent IASL review (Ref. 16). The first published claim for having observed the formation of metallic hydrogen was made by the Soviet shock-wave experimentalists F. V. Grigorev and S. B. Kormer (Refs. 16 and 17) in 1972. The pressure for the transformation was said to be about 2.8 Mbar. The group at Lawrence Livermore Laboratory, as reported by R. S. Hawke (cited in Ref. 9), has recently confirmed, by magnetic compression experiments, that hydrogen shows a metallic-like conductivity at a pressure estimated between 1.5 Mbar and 6.0 Mbar. However, A. K. McMahan (cited in Ref. 10) points out that it is entirely possible that what the LLL group observed was a pressure-induced overlap of the normally filled valence and normally empty conduction bands of solid molecular hydrogen. If so, this would not be a

metastable conductor and, by analogy with "metallic" iodine [unpublished data quoted by B. Matthias (Ref. 9)], would probably not show superconductivity. Thus, the transient metallic state observed by the U.S. (and, presumably, also by the Soviets) may not be a phase of any practical interest.

Nonetheless, the Soviets recently reported (Ref. 19) what might be the first static formation of a metallic phase of hydrogen which appears to show a considerable degree of metastability as the pressure is released. This was a small-scale experiment on a very thin layer of H_2 , carried out at 4.2 K. At a jack load which was estimated to correspond to a pressure between 1 Mbar and 3 Mbar the resistance of a circuit which included the specimen (no experimental details are available) dropped suddenly by a factor of 10^6 . As the load was released, the lower resistance was retained until the load reached about 1/10 or 1/20 of the initial value. This hysteresis was taken to imply that the new phase was metastable to quite low pressures.* It was later stated by Vereshchagin** that the experimental set-up was such that superconductivity could not be measured (Ref. 20); this dismisses, without explanation, the data which superficially indicates that the "electrical resistance of hydrogen" remains finite at 4.2 K. If literally true, this would imply no superconductivity above 4.2 K which, of course, would vastly diminish interest in the metal phase.

It is difficult to evaluate the results of this experiment with the information at hand. It is possible that a band overlap in solid H_2 is being observed and the hysteresis arises

* Even if this is true, the pressures are not low enough to make the "metallic hydrogen" of practical interest. This is why the Soviets talk about further stabilizing the metal phase.

** L. F. Vereshchagin died on 20 February 1977.

in the mechanical equipment (friction effects, etc.). This appears unlikely, since slow pressure cycling and thermal annealing control experiments were carried out which tend to make such a hypothesis improbable. Yakovlev states that these control experiments also remove the possibility of short-circuiting, which is by no means obvious without more details. Another possibility, which cannot be discounted completely, is that the properties of hydrogen are not being measured at all! Vereshchagin (Refs. 16 and 20) has reported the transition of diamond to a metallic carbon phase (of unknown structure) at about 1 Mbar at room temperature. Solid H_2 is so compressible that U.S. researchers have occasionally squeezed samples right out of the apparatus when the seals were slightly imperfect (Ref. 9). It is not inconceivable that, in the Soviet experiment, the H_2 sample was lost and the transition of the carbonado (diamond) anvils to metallic carbon was being measured.

In all their outward comments, the Soviet researchers under Vereshchagin at the Institute of High Pressure Physics, are very optimistic about being able to obtain a truly metastable metallic hydrogen phase at one atmosphere and quite high temperatures. For example, Vereshchagin is quoted (Ref. 20) as saying "from the viewpoint of binding energy, metallic hydrogen is . . . much stronger than all the metals of the periodic table." If the zero-temperature binding energy of 0.8 eV/atom is correct (Ref. 14), this statement is clearly not literally true. Mercury is 0.8 in these units. Zinc is 1.4, Lithium is 2.0, Sodium is 1.3, Potassium is 1.1, etc. Nonetheless, allowing for the obvious hyperbole, it is apparent that Vereshchagin believes metallic hydrogen to have a high degree of metastability (at least of the order of 1 eV/atom) and the main problem is one of quenching it in. He also states firmly that a superconducting T_C of between 200 K to 300 K will be obtained. In terms of his priorities for the short-term research goals of the Institute, Vereshchagin states

(Ref. 20) "the main purpose in the general research program is to produce metallic hydrogen in a large volume and to solve the problem of stabilizing the metallic phase." Thus, without equivocation, he places the solution of the hydrogen problem as the most important near-term objective of his Institute (which performs an estimated 80 percent of all high-pressure research in the Soviet Union). This certainly implies that he has little doubt about the conditions needed to produce the metal phase and is mostly concerned about the engineering problems in operating a new, large (50,000 metric ton) research press which is supposed to be ready momentarily. This press, at an estimated U.S. equivalent cost of \$17 million (Ref. 18), will reportedly apply several Mbars of pressure over a relatively large volume (about 1 cm³) (Ref. 20).

It should be mentioned that there is a lack of unanimity even in the Soviet Union on the success of producing metastable metallic hydrogen. The LASL review (Ref. 16) relates that E. I. Estrin (of the Institute of Metallurgy and Metal Physics) has presented thermodynamic arguments that a metastable metal phase should melt at a lower temperature than solid molecular hydrogen (14 K). S. V. Iordanskii and colleagues (the Landau Institute for Theoretical Physics) have argued, for reasons not known to the writer, that the postulated metallic phase may not have a large binding energy and, in fact, may not have any at all.

It should be pointed out that our present knowledge of the equation of state of molecular hydrogen is poor, except at relatively low pressures. One of the most thorough attempts to calculate the high pressure properties of H₂ was made by R. D. Ethers (Ref. 9) of Colorado State University and he admits that the difficulty in theoretically incorporating many-body interactions make his results very imprecise at high pressures. Part of the problem is attributable to the lack of

good pressure-volume experimental data at pressures higher than about 30 kbar. The LASL authors (Ref. 16) suggest that a systematic and detailed pressure-volume-temperature map is required for hydrogen up to about 100 kbar to 200 kbar pressure and from room temperature to below 1 K. They estimate this would require about 15 to 25 man-years of effort. There is no question that such a careful map of data would be very useful and should be followed by higher pressure (~ 1 Mbar) experimental mapping when proper facilities are available.

A brief word should be said on the question of equipment and calibration of pressure. It is generally accepted (Refs. 16 to 20) that the Soviets succeeded in synthesizing large specimens of carbonado in about 1972, although it is not entirely clear how good and uniform this material is. Carbonado is a dense, small-grained polycrystalline diamond, and Vereshchagin has used anvils of it to produce claimed pressures of over 1 Mbar. Such pressures cannot be obtained by using carbide or lower-quality diamond anvils, widely used at present in the U.S., and it is usually stated that this represents a serious lag in the U.S. ultra-high-pressure technology. However, there are some interesting discrepancies in published pressure calibrations of the U.S., U.S.S.R. and Japan (Refs. 9 and 21). NaCl shows a sharp drop in resistivity (of several orders of magnitude) at a certain critical pressure. The group at the Watervliet Arsenal calibrate this pressure at 290 kbar while the Soviets report this pressure to be 750 kbar (as calibrated on their press used at about 1 Mbar to produce the "metallic hydrogen" transition referred to previously). In other examples, the Watervliet group reported the semiconductor-metal transition of GaP to occur at 216 kbar, while the Japanese reported this near 500 kbar; also, the Watervliet group showed the Bismuth VI-IX transition at 320 kbar, while the Japanese did not detect it up to a reported 400 kbar. Over the last 5 or 6 years, U.S. scientists have spent a great deal of effort on pressure

measurement, and it is now believed with a high degree of confidence, that U.S. calibration techniques are quite accurate, at least up to about 300 kbar. This suggests the possibility that the reported Soviet Mbar pressures are really closer to 400 kbar and that the Japanese are also too high by about a factor of two. This might be significant, since, if true, and if the Soviet data on hydrogen mentioned above (Ref. 19) is really the metallic transition, then metallic hydrogen is actually formed at about 400 kbar, well within the near-term range of the Watervliet equipment. Such an implication could give a strong incentive for the Army to build up to 500 kbar capability as soon as possible.

An alternate approach has been suggested (Refs. 16 and 22) for the formation of metallic hydrogen involving low-temperature dissociation of H_2 to $2H$ by some means such as an electrical discharge. One proposal involved high magnetic fields to maintain the atomic state long enough to permit possible condensation into a metallic state. Experimental work is being pursued, along slightly different lines, at the NASA Lewis Research Center. Here, hydrogen containing some tritium is cooled to about 0.3 K. The beta radiation from tritium decay performs the dissociation, and it is hoped that the low temperature will permit the condensation of the metal state. If successful, such techniques could obviate the need for very high pressure.

A detailed review and analysis of the overall theoretical and experimental problems of metallic hydrogen can be found in a recent RAND report (Ref. 11), which also contains a thorough list of references. This points out that N. Kawai (in Japan) also claims to have produced metallic hydrogen statically; as with the Soviet claim, there is some controversy regarding what was actually observed.

APPENDIX B

HYDRIDES

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HYDRIDES

Appendix A described the technical aspects of pure hydrogen in very dense phases, in particular, a hoped-for metastable metallic state. As noted, there is doubt whether such a state has ever been observed or whether it is even possible (in a usable form). Now, compounds of H with metals have been studied intensively for many years, especially in the 1950s for nuclear technology applications but also, more recently, for energy storage usage. Many of these compounds have high hydrogen densities. For example, TiH_2 has nearly 10^{23} H atoms per cm^3 , reasonably close to the predicted H density of about 4×10^{23} for metallic hydrogen and greater than liquid hydrogen. Thus, there has been recent interest in the question of whether some of the postulated properties of metallic hydrogen (especially high-temperature superconductivity) can be modeled with hydrides.

Gilman (Ref. 6) has suggested an investigation of hydrogen-dielectric compounds. In particular, he has made a preliminary study of the hypothetical material LiH_2F , which is not known as a stable compound at one atmosphere, but for which plausible arguments can be made that it is nearly stable. In fact, rough calculations suggest that LiH_2F should be stable at only a few kbar at liquid nitrogen temperatures.

Basically, Gilman's reasoning is as follows. LiF is an ionic crystal with a rocksalt lattice structure. LiH_2F is conceptually formed by inserting interstitial H atoms in the

(pseudo) octahedral holes, so that the hydrogen sub-lattice is simple cubic. The key point is that the hydrogen is now immersed in a dielectric medium and the energy difference between the molecular and the metallic state of the hydrogen is reduced roughly as the inverse square of the dielectric constant of the LiF. Using the optical dielectric constant of 1.92, he calculates a much lower transformation pressure than that for pure hydrogen only. Unfortunately, his numerical calculations appear to be in error* and the specific material he used as an example may not be promising. Nonetheless, the basic concept looks valid. It is not clear to the writer that only the optical dielectric constant should be used; a closer theoretical look should be taken at the effects of lattice polarization.

The important feature of the above discussion is not necessarily that LiH_2F could show a metallic hydrogen behavior. The chief issue raised, as pointed out by Maksimov (Ref. 23), is that more attention should be paid to hydrogen compounds that are dielectric, particularly those which show a reasonable degree of ionic binding. Compounds which come immediately to mind are those which form with ammonia, including NH_3 itself. Ammonium fluoride, NH_4F , and ammonium hydrogen fluoride, NH_4HF_2 , are typical materials which might be interesting, since they have a high hydrogen content and are normally dielectrics. As another example, boron forms a wide composition of hydrides, starting with diborane (B_2H_6), and progressing down, in terms of relative H content, to $\text{B}_{10}\text{H}_{14}$. There are additional boron-nitrogen hydrides, such as B_2NH_7 . The B-H bonds have a high degree of one-electron character and hence would show ionicity. High-pressure research on such materials could be interesting.

In the metallic hydrides (most of the hydrides of the transition elements, actinides and rare earths are metallic),

* Personal communication from C. F. Cline of Lawrence Livermore Laboratory.

efforts to look for superconductivity, at one atmosphere pressure, have been widespread (Refs. 4 and 23) because of speculation* that a sub-lattice of metallic hydrogen would form and contribute a high T_C . Superconducting hydrides were not found until 1970, when the Illinois group (Ref. 4) first showed that a higher hydride of thorium (Th_4H_{15}) was a superconductor with a T_C of about 8 K (note that ThH_2 does not show superconductivity; pure thorium has a T_C of about 1.4 K). The deuteride was also measured, but there was no evidence of an isotope effect, a fact that is still not completely understood. In 1972, Skoskiewicz (Ref. 24) found that PdH became superconducting at 9 K, which was surprising, since Pd is not a superconductor. Moreover, PdD has a T_C of 11 K, which is an isotope effect in the wrong direction. Considerable work since then has been done on hydrides (and deuterides) of Pd alloyed with Cu, Ag, Au, Ni, Pt, and Rh. The increasing addition of the noble metals (Cu, Ag, and Au) increases the T_C to a maximum value, after which the T_C decreases. The highest T_C reported is the hydride of $\text{Pd}_{55}\text{Cu}_{45}$ (in atomic percent) with a value of nearly 17 K. Also, the variation of T_C with H and D concentration for unalloyed Pd has led to the suggestion (Ref. 25) that the reverse isotope effect is due to the higher average amplitude of the H atom vibrations (as opposed to the heavier D atom), which makes the electronic interaction between Pd and H atoms greater than between Pd and D. It is shown that this is in the proper direction to explain the isotope anomaly and also the somewhat greater lattice constant for the deuteride. Unfortunately, later work on Pd-Ag alloys shows that the isotope effect decreases as Ag is added, becomes zero for the composition $\text{Pd}_{85}\text{Ag}_{15}$, and then

*This idea, incidentally, has not been experimentally supported to date.

reverses itself (i.e., shows the normal behavior) as more silver is added. This cannot be correlated with the above idea alone and it is clear that the situation requires a more complex theory, possibly involving the optical modes.

The behavior of T_C with moderate pressures (20 kbar to 30 kbar) has been examined for both Th_4H_{15} and PdH . For Th_4H_{15} , T_C goes *up* with pressure (Ref. 26) at a rate of 30 mK per kbar. For PdH , T_C goes *down* with pressure (Ref. 25) at just about the same rate. Except for some transient measurements on lithium hydride isotopes, this data appears to be the *only* information reported on the pressure dependence of *any* of the hydrides. Even for these materials, it would be interesting to extend the pressure range, especially for the thorium hydride system. This system is sufficiently complex that one would almost expect new phases at higher pressures. Also, it is tempting (although admittedly without much hard justification) to suggest work on thorium-yttrium hydrides. This system might be analogous to the yttrium-thorium sesquicarbide material, $(\text{Y}_{.7}\text{Th}_{.3})_2\text{C}_3$, recently synthesized (Ref. 8) by the Los Alamos group at about 25 kbar. It has a body-centered-cubic structure, is metastable at one atmosphere, and exhibits a T_C of 17 K.

Although we did not find published information on the subject, there has been speculation by researchers that hydrides may be useful as surface catalysts in attempting to grow metallic hydrogen from solid H_2 under pressure. Merely placing a material under pressure where another phase is preferred does not ensure that the phase transition will actually occur in a practical time frame. The kinetics must be considered for the nucleation and growth of the new equilibrium state compared to the original state (and, for that matter, any other states that might exist nearby on the phase diagram). The nucleation process is usually the pacing step; once nuclei of critical size are formed, further growth proceeds relatively

easily. The formation work for nucleation was qualitatively examined by Neuhaus (Ref. 27) in the context of the graphite-diamond transition. If one is close enough to the phase boundary line to make the vapor pressures of the two phases essentially equal, he finds that the energy required for nucleation is proportional to the density of the phase being nucleated. This means that the state with the lower density will preferentially nucleate, even if it is not stable in an equilibrium sense. If the densities of the two phases do not differ by much, there is little effect, since there will be enough nuclei formed of the new state to permit the transformation to proceed readily. However, in the case of carbon studied by Neuhaus, the density of graphite is 30 percent less than that of diamond and his conclusion was that the transformation could not proceed, in any practical sense, unless the pressure was very much higher than the critical transition pressure. For the case of hydrogen, the density of solid H_2 at pressures around 1 Mbar is not known with any accuracy, but it is almost certainly much less than that of the metallic phase. Therefore, it is possible that any practical method of producing metallic hydrogen (assuming it can be produced at all) would require the presence of a catalyst, most likely a fine powder of a hydride-forming material which could already be in a hydride state. For research purposes, at least, this hydride-former should probably be a dielectric to facilitate measuring changes in electrical resistivity.